JC14 Rec'd

FORM PTO-1390 (REV 9-2001) U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY 'S DOCKET NUMBER
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		24180-653001
		U S APPLICATION NO (If known, see 37 CFR 1 5) unassigned 10/018322
INTERNATIONAL APPLICATION NO. PCT/IB00/00934	INTERNATIONAL FILING DATE 6 June 2000 (06.06.2000)	PRIORITY DATE CLAIMED 11 June 1999 (11.06.1999)

TITLE OF INVENTION
BARRIER MATERIAL MADE OF EXTRUDED MICROLAYERS

APPLICANT(S) FOR DO/EO/US
Tournier, et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. [x] This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. [ ] This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. [x] This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. [ ] The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. [x] A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. [ ] is attached hereto (required only if not communicated by the International Bureau).
   b. [x] has been communicated by the International Bureau.
   c. [ ] is not required, as the application was filed in the United States Receiving Office (RO/US).
6. [x] An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
   a. [ ] is attached hereto.
   b. [x] has been previously submitted under 35 U.S.C. 154(d)(4).
7. [ ] Amendments to the claims of the International Aplication under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. [ ] are attached hereto (required only if not communicated by the International Bureau).
   b. [ ] have been communicated by the International Bureau.
   c. [ ] have not been made; however, the time limit for making such amendments has NOT expired.
   d. [ ] have not been made and will not be made.
8. [ ] An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. [x] An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. [ ] An English lanugage translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. [x] An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. [ ] An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. [x] A FIRST preliminary amendment.
14. [ ] A SECOND or SUBSEQUENT preliminary amendment.
15. [ ] A substitute specification.
16. [ ] A change of power of attorney and/or address letter.
17. [ ] A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. [ ] A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. [ ] A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. [ ] Other items or information:

U.S. APPLICATION NO (if known, see 37 CFR 1.5) 10/018522 unassigned	INTERNATIONAL APPLICATION NO PCT/IB00/00934	ATTORNEY'S DOCKET NUMBER 24180-653001

21. ☒ The following fees are submitted:

	CALCULATIONS PTO USE ONLY	
BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):		
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO **$1040.00**		
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO **$890.00**		
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO **$740.00**		
International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) **$710.00**		
International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) **$100.00**		
ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 890	
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(e)).	$	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	28 - 20 =	8	x **$18.00**	$ 144	
Independent claims	2 - 3 =	0	x **$84.00**	$	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ **$280.00**	$	
TOTAL OF ABOVE CALCULATIONS =				$ 1,034	
☐ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2. +				$	
SUBTOTAL =				$ 1,034	
Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				$	
TOTAL NATIONAL FEE =				$ 1,034	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00** per property +				$	
TOTAL FEES ENCLOSED =				$ 1,034	
				Amount to be refunded:	$
				charged:	$

a. ☐ A check in the amount of $ _____ to cover the above fees is enclosed.

b. ☒ Please charge my Deposit Account No. 13-0206 in the amount of $ 1,034 to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. _____. A duplicate copy of this sheet is enclosed.

d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:
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227 West Monroe Street
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US

SIGNATURE

Stephen T. Scherrer
NAME

45,080
REGISTRATION NUMBER

PATENT
Docket No. 24180-653001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re U.S. Patent Application of: Tournier, et al.	
Appln. No.:	attached hereto
Filed:	December 11, 2001
For:	**BARRIER MATERIAL MADE OF EXTRUDED MICROLAYERS**
Examiner:	Unassigned
Art Unit:	Unassigned

PRELIMINARY AMENDMENT

Box: New Patent Application
Assistant Commissioner for Patents
Washington, D.C. 20231

Dear Sir:

This paper is being submitted simultaneously with the filing of a new application. Applicant respectfully requests entry of this paper prior to examination of this application on its merits.

Please amend the present application as follows:

In the Claims:

6. (Amended) The film of Claims[s] 4 [or 5] wherein at least one of the thermoplastic materials is selected from the group consisting of polyamide, polyethylene and polypropylene.

7. (Amended) The film of Claim[s] 4 [or 5] further comprising:

at least one adhesive microlayer between the first and second microlayers in each recurring unit wherein the adhesive microlayer bonds the first microlayer to the second microlayer.

10. (Amended) The film of [any of] Claim[s] 1[-9] further comprising:

an external layer disposed on a surface of the stack of microlayers.

15. (Amended) The film of Claim[s] 7 [or 8] wherein the adhesive microlayers are partially soluble at the same time to the microlayers surrounding the adhesive microlayers.

16. (Amended) The film of Claim[s] 3 [or 9] wherein the first and second thermoplastic materials are selected from the group consisting of polyamide and ethylene-vinyl alcohol copolymer.

Please add the following new claims:

18. (New) The film of Claim 5 wherein at least one of the thermoplastic materials is selected from the group consisting of polyamide, polyethylene and polypropylene.

19. (New) The film of Claim 5 further comprising:

at least one adhesive microlayer between the first and second microlayers in each recurring unit wherein the adhesive microlayer bonds the first microlayer to the second microlayer.

20. (New) The film of Claim 2 further comprising:

an external layer disposed on a surface of the stack of microlayers.

21. (New) The film of Claim 3 further comprising:

an external layer disposed on a surface of the stack of microlayers.

22. (New) The film of Claim 4 further comprising:

an external layer disposed on a surface of the stack of microlayers.

23. (New) The film of Claim 5 further comprising:

an external layer disposed on a surface of the stack of microlayers.

24. (New) The film of Claim 6 further comprising:

an external layer disposed on a surface of the stack of microlayers.

25. (New) The film of Claim 7 further comprising:

an external layer disposed on a surface of the stack of microlayers.

26. (New) The film of Claim 8 further comprising:

an external layer disposed on a surface of the stack of microlayers.

27. (New) The film of Claim 9 further comprising:

an external layer disposed on a surface of the stack of microlayers.

28. (New) The film of Claim 8 wherein the adhesive microlayers are partially soluble at the same time to the microlayers surrounding the adhesive microlayers.

29. (New) The film of Claim 9 wherein the first and second thermoplastic materials are selected from the group consisting of polyamide and ethylene-vinyl alcohol copolymer.

REMARKS

This paper is being filed simultaneously with a request to begin National Examination Procedures under 35 U.S.C. 371 of International Patent Application No. PCT/IB00/00934 filed on June 6, 2000. Applicants respectfully request entry of the instant amendment prior to examination of the requested national application on its merits and prior to calculation of the filing fees for the requested national application. No new matter has been added by this Amendment.

In re Appln. of Tournier, et al.
U.S. National Phase of PCT/IB00/00934

Attached hereto is a marked-up version of the changes made to the claims by this paper and a clean version of the amended claims. The attached pages are captioned "Version With Markings To Show Changes" and "Clean Version of Amended Claims".

Respectfully submitted,

Stephen T. Scherrer, Reg. No. 45,080

Date: December 11, 2001

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fax. no. (312) 984-7700

Version with Markings to Show Changes

In the Claims:

Please amend the claims as follows:

6. (Amended) The film of Claim[s] 4 [or 5] wherein at least one of the thermoplastic materials is selected from the group consisting of polyamide, polyethylene and polypropylene.

7. (Amended) The film of Claim[s] 4 [or 5] further comprising:

at least one adhesive microlayer between the first and second microlayers in each recurring unit wherein the adhesive microlayer bonds the first microlayer to the second microlayer.

10. (Amended) The film of [any of] Claim[s] 1[-9] further comprising:

an external layer disposed on a surface of the stack of microlayers.

15. (Amended) The film of Claim[s] 7 [or 8] wherein the adhesive microlayers are partially soluble at the same time to the microlayers surrounding the adhesive microlayers.

16. (Amended) The film of Claim[s] 3 [or 9] wherein the first and second thermoplastic materials are selected from the group consisting of polyamide and ethylene-vinyl alcohol copolymer.

Please add the following new claims:

18. (New) The film of Claim 5 wherein at least one of the thermoplastic materials is selected from the group consisting of polyamide, polyethylene and polypropylene.

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29. (New) The film of Claim 9 wherein the first and second thermoplastic materials are selected from the group consisting of polyamide and ethylene-vinyl alcohol copolymer.

Clean Version of Amended Claims

6. The film of Claim 4 wherein at least one of the thermoplastic materials is selected from the group consisting of polyamide, polyethylene and polypropylene.

7. The film of Claim 4 further comprising:

at least one adhesive microlayer between the first and second microlayers in each recurring unit wherein the adhesive microlayer bonds the first microlayer to the second microlayer.

10. The film of Claim 1 further comprising:

an external layer disposed on a surface of the stack of microlayers.

15. The film of Claim 7 wherein the adhesive microlayers are partially soluble at the same time to the microlayers surrounding the adhesive microlayers.

16. The film of Claim 9 wherein the first and second thermoplastic materials are selected from the group consisting of polyamide and ethylene-vinyl alcohol copolymer.

18. The film of Claim 5 wherein at least one of the thermoplastic materials is selected from the group consisting of polyamide, polyethylene and polypropylene.

19. The film of Claim 5 further comprising:

at least one adhesive microlayer between the first and second microlayers in each recurring unit wherein the adhesive microlayer bonds the first microlayer to the second microlayer.

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an external layer disposed on a surface of the stack of microlayers.

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an external layer disposed on a surface of the stack of microlayers.

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an external layer disposed on a surface of the stack of microlayers.

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BARRIER MATERIAL MADE OF EXTRUDED MICROLAYERS

FIELD OF THE INVENTION

The present invention relates to a barrier material for a flexible film or tape constructed of multilayer materials. Specifically, the present invention relates to a multilayer material constructed of extruded microlayers capable of being a barrier to gases and vapor such as, for example, oxygen, water vapor and/or flavors.

BACKGROUND OF THE INVENTION

It is, of course, generally known to utilize a multilayer film as a barrier layer. Generally, the multilayer film may be useful in packaging to limit the exchange of gas or vapor molecules between two discrete volumes such as, for example, between the outside air and an inside atmosphere of a package. Specifically, humidity and oxygen tend to degrade the quality of a packaged product, such as, for example, foods by diffusing across the packaging film. Further, flavors can be lost if diffused through the packaging film to the outside air.

It is also generally known to utilize polyolefin material as barrier layers in film packaging products. Typical polyolefins may consist of polyethylene ("PE"), polypropylene ("PP") and polyethylene terephthalate ("PET"). Other polymers or copolymers that may be utilized as barrier layers in film packaging products may include ethylene-vinyl alcohol ("EVOH"), polyvinylidene chloride ("PVDC"), polyamides ("nylon", "PA6" or "MXD6"), polyketones and other like polymeric material. However, many of these barrier materials may have certain drawbacks. For example, in the case of EVOH, it is known that these polymers are sensitive to humidity and must be protected therefrom. However, protecting EVOH from humidity may cause a reduction in the barrier properties of the EVOH material. The typical multilayer films based on EVOH thus contain at least three or more layers (usually five) including one barrier layer of EVOH, two external layers "A" and "C", and two layers of adhesive

("Adh"), to ensure the connection between the EVOH and the external layers. This arrangement of film layers may be represented symbolically by the following structure: A/Adh/EVOH/Adh/C with "/" representing the division between the layers.

Further, it is generally known to improve mechanical properties of films by incorporating a polyamide layer such as, for example, a layer consisting of PA6 to protect the barrier layer from damaging water vapor. Such a film can be represented by the structure A/Adh/PA6/EVOH/PA6/Adh/C.

Much research, therefore, is currently being conducted to improve existing films. Generally, the object of this research is to improve the technical quality while maintaining economic feasibility. Specifically, technical quality may include the layers' ability to withstand the diffusion of gas or vapor molecules and the ability to resist pinholing, cracking or other degradation due to stress on the films. In addition, technical quality of the films may include other mechanical properties of the films while in use.

Still further, it is known to use a technique of microlayer-extrusion to create specific films. This technique of microlayer-extrusion is described in the article of J. Im and W.J. Schrenk entitled "Coextruded Microlayer Film and Sheet" published in "The Journal of Plastic Film & Sheeting", Vol. 4, April 1988, pages 104 to 115. This article describes the technique for creating ultraviolet ("UV") reflective films made up of coextruded microlayers consisting of a polypropylene ("PP") and a polycarbonate ("PC"), each microlayer having the configuration "PP/PC". In addition, the article describes ultra-narrow films of PC that can function as a dielectric layer in capacitors. Specifically, the article describes the mechanical properties and the impact stability of films made from coextruded microlayers that alternate a layer of ductile material (PC) and a layer of brittle material such as, for example styrene-acrylonitrile copolymer ("SAN"). This technique is also mentioned in U.S. Patent No. 4,965,135, for which J. Im is an inventor. The '135 patent describes a film having improved bending properties made from an alternation of co-extruded microlayers of a ductile material (polyamide) and a brittle material (polystyrene).

This technique of microlayer-extrusion is also used in U.S. No 3,576,707, for which W.J. Schrenk is an inventor, to make iridescent plastic articles by coextrusion of two polymers having a significant difference of their refractive index.

This technique of microlayer-extrusion is also used in U.S. No 5,269,995 for which W.J. Schrenk is an inventor, to make reflective plastic bodies by coextrusion of two polymers having a significant difference of their refractive index, and extrusion of a third polymer as skin protective layer.

A need, therefore, exists for an improved barrier material for a flexible film packaging or tape that provides for the prohibition of molecular diffusion of gases and vapors therethrough while maintaining superior mechanical characteristics.

SUMMARY OF THE INVENTION

The present invention relates to a barrier layer for flexible film packaging or tape made from a plurality of extruded microlayers. Specifically, the invention relates to combinations of structural materials, barrier materials for water vapor and humidity, and/or barrier materials for oxygen-proofing by a process of extrusion of microlayers.

While many materials may be utilized in the creation of the barrier layer using microlayers, the present invention highlights the possibility of making a film from a single barrier material formed from coextruded microlayers. In fact, by increasing the number of layers of barrier material and by reducing the thickness of the layers to preserve a constant total thickness of the barrier layer, an increase in the mechanical properties, such as, for example, flex cracking, was observed with little to no reduction in the barrier properties.

The structural materials that may be utilized for the barrier layer may include, for example, polyolefines such as low density polyethylene ("LDPE"), linear low density polyethylene ("LLDPE"), high density polyethylene ("HDPE"), metallocene polymers, PP, copolymers or mixtures of polyolefins, polystyrene and/or copolymers, polyesters or copolyesters, polyamides, acrylic and methacrylic polymers and copolymers, polycarbonates, thermoplastic polyurethanes, liquid crystalline polymers ("LCP"), and other technical polymers. Further, barrier materials that may be utilized specifically against humidity or water vapor may include polymers or copolymers based on: EVOH, PVDC, PA6, MXD6, polyketones, LCP, or other like materials. Of course, any material may be utilized as a barrier material that may be apparent to those skilled in the art.

It is, therefore, an advantage of the present invention to provide a multilayer film and a method of manufacturing the film that provide a large variety of films having diverse properties and further have good to excellent mechanical and barrier properties.

Further, it is an advantage of the present invention to provide a multilayer film and a method of manufacturing the film that increase greatly the supply of a variety of different films for particular needs. Still further, it is an advantage of the present invention to provide a multilayer film and a method of manufacturing the film that are economical but have the same or similar barrier and/or mechanical properties relative to known barrier layers.

Moreover, an advantage of the present invention is to provide a multilayer film and a method of manufacturing the film that reduce the materials needed for the production of the multilayer material by removing layers or reducing layers' thicknesses without a significant increase in costs of manufacturing. And, an advantage of the present invention is to provide a multilayer film and a method of manufacturing the film that can be utilized on standard extrusion or coextrusion equipment. Further, an advantage of the present invention is to provide a multilayer film and a method of manufacturing the film that may improve optical properties including, but not limited to filters (UV or visible), waveguides, iridescent materials and materials having controlled opaqueness.

In addition, an advantage of the present invention is to provide a multilayer film and a method of manufacturing the film that may improve mechanical properties, including, but not limited to, deadfold, chemical delamination, resistance to puncture, the ability for improved thermoforming, improved thermal stability to sterilization and heat filling and biaxial or uniaxial orientation. Moreover, an advantage of the present invention is to provide a multilayer film and a method of manufacturing the film that may improve barrier properties including, but not limited to, loading of inserts, control of the structure in the solid state, effect of controlled diffusion, exfoliation of submicron mineral filler and a controlled absorption.

Also, an advantage of the present invention is to provide a multilayer film and a method of manufacturing the film that may improve electrical properties such as, for example, conducting charges and/or creating polymer conductors leading to anisotropic conductance and antistatic properties. And, an advantage of the present invention is to provide a multilayer film and a method of manufacturing the film that may improve surface properties to make active systems with reactive layers, controlled diffusion ensuring supply of an additive or a medication, activation by irradiation or thermal

treatment and properties of adsorption and/or trapping of molecules. Moreover, an advantage of the present invention is to provide a multilayer film and a method of manufacturing the film that may be shaped into three-dimensional applications such as, for example, tubes, laminates, laminated sheets, stamped containers, trays, boxes and/or products molded by laminar injection.

Additional features and advantages of the present invention are described in, and will be apparent from the detailed description of the presently preferred embodiments and from the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a stress vs. strain diagram relating to five films having microlayers of PA6 with a number of microlayers $p = 2^n$ with n equal to 1, 5, 6, 7 and 8.

Figure 2 shows a stress vs. strain diagram relating to five films having microlayers of EVOH with a number of microlayers $p = 2^n$ with n equal to 1, 5, 6, 7 and 8.

Figure 3 shows a stress vs. strain diagram relating to six films having an alternation of microlayers consisting of PA6 and EVOH, roughly 50/50 by volume, and with a number of microlayers $p = 2^n$ with n equal to 1, 5, 6, 7, 8, and 11.

Figure 4 is a diagram showing resistance to flex cracking measured by the number of holes after bending as a function of the number p of microlayers (represented logarithmically). "I" corresponds to a film made up of microlayers of EVOH. "II" corresponds to a film made of microlayers of PA6. "III" corresponds to a film of PA6/EVOH 50/50 by volume, and made of an alternation of microlayers of PA6 and microlayers of EVOH of the same thickness. And "IV" corresponds to a film of PA6/EVOH 90/10 by volume, made up of an alternation of microlayers of PA6 and microlayers of EVOH, the microlayers of PA6 having thicknesses 9 times larger than the thicknesses of the microlayers of EVOH.

Figure 5 is a diagram showing, for the same films as those tested in Figure 4, the progress of oxygen permeability as a function of the number p of microlayers.

Figure 6 is a diagram showing, for the same films as those tested in Figures 4 and 5, the progression of resistance to puncture in MPa as a function of the number p of microlayers.

Figure 7 is a histogram showing the values of four parameters relating to the film PA6/EVOH--50/50 by volume that is identical to the film III of Figure 4 as a function of the number n corresponding to the number of layers p ($p = 2^n$) of microlayers of film PA6/EVOH--50/50 by volume. The four parameter include: 1) the enthalpy of fusion of PA6; 2) the enthalpy of fusion of EVOH; 3) the percentage by weight of the interface compound between each microlayer of PA6 and each microlayer EVOH determined from IR spectra; and 4) the oxygen permeability of the film having microlayers PA6/EVOH--50/50 by volume.

Figures 8 is a stress vs. strain diagram showing the effect of the composition of the mixture PA6+EVOH on the mechanical characteristics of the film made up of a single layer of the mixture.

Figure 9 shows a stress vs. percent by volume of PA6 diagram further indicating the effect of the composition of the mixture of PA6+EVOH on the mechanical characteristics of the film made up of a single layer of the mixture.

Figure 10 shows a strain vs. percent by volume of PA6 diagram further indicating the effect of the composition of the mixture of PA6+EVOH on the mechanical characteristics of the film made up of a single layer of the mixture.

Figure 11 shows a diagram of a differential scanning calorimetry ("DSC"), with the enthalpy H shown as a function of the temperature T in °C for EVOH and PA6. Figure 11 further shows a variable volume percentage of EVOH and PA6, from 100/0.

Figure 12 shows a diagram of the DSC with the enthalpy H shown as a function of T in °C. Further, Figure 12 shows a variable number n corresponding to the number $p=2^n$ of microlayers (for a proportion EVOH/PA6--50/50 by volume).

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention relates to a multilayer film and a method of manufacturing the same that may be utilized as a barrier layer against gas and vapors. Generally, the present invention relates to a barrier layer film or tape that may be constructed from a plurality of microlayers, each of the microlayers coextruded thereby providing increases in mechanical properties while having little to no loss in performance of barrier properties.

According to the invention, the multilayer film may consist of a stack of microlayers $(X)_p$, having at least $p = 2^n$ units of extruded microlayers of thermoplastic material where p may represent the total number of microlayers and n may represent any whole number. Further, $(X)_p$ may represent the thickness of the stack having the structure "X/X/X..." with p times the same unit X and each unit of the structure being symbolically separated from the adjacent layer by the sign " / ". While n can be any whole number, favorable results tend to occur when n is at least 4 or 5. Further, the material may form a film or a tape having a total thickness of between 10 and 2500 μm.

Each unit X may consist of one or more microlayers. If more than one microlayer is contained within each unit, then the microlayers may be coextruded together. In addition, each barrier microlayer within each unit X may be represented by "b" and may be a barrier against oxygen and/or water vapor. Alternatively, the barrier microlayer b may consist of a mixture of barrier materials.

Generally, the term "film" may be used to denote material that consists of microlayers according to the invention or that comprises microlayers according to the invention. Of course, "film" may refer to film in the narrow sense. However, other thicker materials (typically above 300 μm) may be included under the general term "film." Further, the general term "film" may include films having standard layers that are produced using a coextrusion or lamination technique that does not utilize microlayers. Typically, such a "film" may contain a barrier layer, consisting of the plurality of microlayers, having a thickness that is relatively equal to the thickness of a standard film containing a single barrier layer.

In a first embodiment of the present invention, the thermoplastic material may be a barrier material against oxygen molecules. Specifically, the barrier microlayer b may be selected from among EVOH, polyketones, PA6, MXD6, PVDC, PLC, polyvinyl alcohol ("PVOH") or any other like barrier material against oxygen that may be apparent to those skilled in the art. Therefore, the barrier layer may be represented by a plurality of layers "b_p" that may be coextruded together. The total number of microlayers p, as noted above, may be represented by $p=2^n$ where n is any whole number. For example, tests using EVOH as a barrier material against oxygen and arranged so that a plurality of microlayers of EVOH are coextruded as a barrier layer indicate, surprisingly, that the

film made therefrom has a resistance to puncture that increases sharply for a number p of microlayers greater than around 25. This corresponds to a number n at least equal to 5 (See Figure 6).

According to a first variation of the invention, each layer "b" may be replaced by a "colayer" having two microlayers "a/b" arranged so as to obtain a stack of units "$(a/b)_p$". Microlayer a may be selected from among PA6, PE, PP or any other material that may be apparent to those skilled in the art. In fact, microlayer "a" may be chosen so as to add an additional property such as, for example, a mechanical characteristic or a different barrier property. Accordingly, films that may be utilized according to this variation may consist of stacks of units of the following: $(PE/EVOH)_p$, $(PP/EVOH)_p$, $(PA6/EVOH)_p$, $(PET/EVOH)_p$, $(PVC/EVOH)_p$ and any other microlayer combination that may be apparent to those skilled in the art to obtain the particular characteristics of the barrier layer desired. Preferably, a material that has a good barrier property against water vapor may be used.

According to a second variation of the invention, each unit may have three microlayers "a/b/c" arranged in a manner so as to obtain a stack of units "$(a/b/c)_p$", in which "c" is selected from among PA6, PE, PP or any other like polymeric material. The microlayer c can be made of a material that is different or the same as the microlayer a. However, in a preferred embodiment, the microlayer c may be different from the microlayer a.

As noted above, however, the microlayer c may be the same as the microlayer a so that the barrier layer may consist of three microlayers "(a/b/a)". For example, EVOH is sensitive to humidity so it may be preferable to coextrude blocks of the type $(a/b/a)_p$, where a designates a material such as PE, PP, PA6, PET, PVC, or any other like material, and b is a layer of EVOH that may then stay inserted between two microlayers a. $(EVOH)_p$ microlayers may be tested in a laboratory by preserving them in a dry atmosphere, such as, for example, in a dessicator, and then testing them quickly before hydration of the film. The EVOH microlayers of Figure 6 (curve 1) were tested in this manner.

Figures 3 to 6 show the properties of the films having units of PA6/EVOH/PA6, for different volume ratios. For example, Figures 4-6 show properties for PA6/EVOH--

90/10 by volume (curve IV) signifying that the microlayers of PA6 are 9 times thicker than the EVOH microlayers. As shown in Figure 3, the mechanical properties (stress and strain) of the PA6/EVOH--50/50 by volume are superior to those of each of the individual components PA6 and EVOH, as shown in Figures 1 and 2. Further, the film having alternating microlayers may have a positive synergistic effect. A same positive synergy may also be seen on standard films consisting of simple mixtures PA6+EVOH (whereby equal volumes of PA6 are mixed with EVOH before coextrusion of the barrier layer) as shown in Figures 8 to 10.

But the comparison of Figures 3 and 8 shows the significant difference of the properties between a standard film and a film having microlayers according to the present invention, each having equal volumes of PA6 and EVOH. Thus, for a same overall composition of EVOH/PA6--50/50 by volume, it has been observed that the films have a yield strength of 120 Mpa for a standard film (Figure 9) and of 160 Mpa for a film according to the invention having 2048 (n=11) microlayers (Figure 3). Further, an elongation of 200% for a standard film with a composition of EVOH/PA6--50/50 by volume (Figure 10) and of 235% for a film according to the invention having 2048 microlayers is seen. These differences are relatively significant.

The formation of thinner and more numerous microlayers can lead to particularly advantageous properties, the majority of which are not predictable, such as for example, the increase in the resistance to puncture shown in Figure 6.

According to a third variation of the invention, each unit having two microlayers "a/b" may include an adhesive microlayer arranged in a manner to obtain a stack of units of type "$(a/d/b)_p$". Preferably, the adhesive microlayers are partially soluble at the same time to the microlayers surrounding the adhesive microlayers. Further, each unit having three microlayers "a/b/c" may include one or two adhesive microlayers arranged in a manner to obtain stacks of units either having five microlayers "$(a/d/b/e/c)_p$", or having four layers "$(a/d/b/c)_p$", or "$(a/b/e/c)_p$", in which "d" and "e" are microlayers of the aforementioned adhesives. Specifically, extrudable adhesives may be desired.

This variation of the present invention may be useful in the case of films for which delamination between the microlayers is particularly not desired. In fact, if, for example, the microlayers a and b or b and c are not or are barely compatible with each

other, the film may consist of microlayers that may be delaminable by including the adhesive layers. However, it has been observed that a film $(a/b)_p$ made up of microlayers according to the invention generally has much less delamination than the standard barrier formed from two layers.

According to the present invention, a film having a recurring unit of five microlayers $(a/d/b/e/c)_p$ may be created, whereby the microlayer b may be EVOH, and microlayers d and e may be made of an extrudable adhesive, and microlayers a and c may typically be made of PE or PP. Of course, other materials may be used as each individual microlayer a, b, c, d or e as may be apparent to those skilled in the art. This invention should not be limited as herein described.

In some cases, it may be advantageous to have units of seven layers "a/f/d/b/e/g/c" consisting of additional microlayers "f" and "g" that are also adhesive materials as well. The microlayers f and g, however, may be selected so as to improve the compatibility and the adherence between the layers a and d and the layers c and e.

According to another embodiment of the present invention, each of the previous films can be modified in the following manner: each unit may be a microlayer "a+b" made of a mixture of the two materials such as, for example, EVOH and PA6. A film, thus, may be represented by a stack of units "$(a+b)_p$".

Further, a film having a recurring unit of three microlayers "a/b/c" may be converted into a film with a recurring unit of two microlayers, such as "a+b/c". In this case, to make the film, two extruders may be sufficient rather than the three that would be needed for "a/b/c". For example, the unit "a+b" of a mixture of two materials may consist of PA6 and EVOH, with a volumetric content of PA6 preferably going from 30 to 90%, and typically equal to 50%. Several phenomena have been observed with this type of microlayer (See figures 8 to 10). First, the advantageous effects of synergy with regard to the mechanical characteristics may be observed. Second, the formation of a reaction product between PA6 having the formula $[-NH-(CH_2)_5-CO-]_x$ and EVOH having the formula $[-(CH_2)_2-CH_2-CHOH-]_y$ by a dehydration reaction between an OH group of the EVOH and an H atom of the amide function of PA6 may be observed. This may cause an increase in the permeability of the film due to a reduction in the crystallinity of the barrier layer. Figure 7 shows an increase in the content of the

reaction product with an increase in the number of microlayers, and the corresponding increase in the permeability of the films. A solution to this problem may be engineering the machinery so as not to produce the reaction products or by using materials that do not react together when mixed.

In an alternate embodiment of the present invention, the film produced by the microlayer barrier layer may include at least one external layer "A" and/or "C", arranged in a manner so as to obtain a structural material "A/$(X)_p$/C" or "A/$(X)_p$" or "$(X)_p$/C" in which "$(X)_p$" represents the stack of microlayers and is selected from among "b", "a/b", "a+b", "a/b/c", "a+b/c", "a/d/b", "a/d/a+b", "a/d/b/c", "a/d/a+b/c", "a/b/e/c", "a+b/e/c", "a/d/b/e/c", "a/d/a+b/e/c" or any other configuration that may be apparent to those skilled in the art. The external layers A and C may be selected from among PA6, PE, PP or other like material. Further, the layer C can be the same or different from the layer A. The layers A and C may be selected for the purpose of fulfilling certain specific functions such as, for example, sealing.

In this embodiment, the layers A and/or C in the films "A/$(X)_p$/C" or "A/$(X)_p$" or "$(X)_p$/C" may not be microlayers, but standard layers. In fact, these films that are made from the stack of microlayers $(X)_p$ that have layers A and/or C laminated or extruded thereon in the traditional manner thus have a "standard" thickness than can typically go from 5 to 50 μm. In contrast, the thicknesses of the microlayers may typically be less than 1 μm.

In a variation of this embodiment, the film may comprise an adhesive layer "D" that may be disposed between the outside layer "A" and the stack $(X)_p$. Further, an adhesive layer "E" may be disposed between the stack $(X)_p$ and the external layer C and arranged in a manner so as to form a structural material "A/D/$(X)_p$/E/C", "A/D/$(X)_p$/C", "A/$(X)_p$/E/C", "A/D/$(X)_p$" or "$(X)_p$/E/C" in which D and/or E may be extrudable adhesives.

Accordingly, a film having the structure "A/D/$(b)_p$/E/C" where the stack of microlayers "b" includes microlayers of EVOH may be constructed. This film may retain roughly the same barrier properties against oxygen and have the mechanical characteristics that may correspond to those of the film "A/D/PA6/EVOH/PA6/E/C", the EVOH barrier layer being a standard single layer material.

Thus, the section "PA6/EVOH/PA6" of this film may be replaced by a stack $(b)_p$ of microlayers consisting of EVOH, having the same thickness of the standard layer of EVOH of the standard film. However, there may be a significant economic advantage in using the EVOH microlayers in that there is a removal of the PA6 layers. This may reduce the amount and number of materials to be extruded and thus the complexity of the extrusion equipment.

The films created by the microlayer barriers may further be constructed of a barrier material against water vapor. This material may be selected from among the polyolefins, such as, for example, PE, PP, the thermoplastic polyesters, PVC, PVDC, PET and/or other like polymeric material.

As previously seen, certain films may comprise layers or microlayers selected from among adhesives, typically extrudable adhesives. These adhesives may contain polyolefins grafted by acid and/or anhydride groups, such as, for example PE or PP grafted by acrylic or maleic groups or other polymers or copolymers.

As is known, identical products may be used for different purposes. Thus, for example, PA6 may be a barrier to oxygen. However, PA6 may also be utilized for its mechanical characteristics.

A further object of the present invention may consist of a process for manufacturing a material or film, The process may comprise the following steps:

First, the stack $(X)_p$ may be manufactured using as many extruders as the number of different microlayers of the unit "X". Further, mechanisms for uniting the flows of these different materials to make a multilayer film may be utilized. A number n of multipliers or mechanisms may be used for doubling the layers of the block in such a manner as to obtain a stack of at least $p = 2^n$ layers. Further, cooling mechanisms for the film at the output of the extruder may be utilized, in which a cooling speed is selected such that the crystallinity of the barrier material is at least equal to 50%.

Second, the structural film "$A/(X)_p/C$", "$A/(X)_p$", "$(X)_p/C$", "$A/D/(X)_p/E/C$", "$A/D/(X)_p/C$", "$A/(X)_p/E/C$", "$A/D/(X)_p$" or "$(X)_p/E/C$" may be manufactured by the bonding to the stack $(X)_p$ of the layers, most of them being external layers, made by lamination or extrusion of the materials A, C, D, E according to the structure desired.

It may be advantageous for the films to not cool rapidly so that the microlayers, specifically the microlayers of EVOH, are allowed to recrystallize and thus improve the mechanical and barrier properties.

EXAMPLE SET 1

1) Manufacturing of the films:

Using equipment for extruding microlayers as described in Schrenk and Alfrey, Jr, "Coextruded Multilayer Polymer Films and Sheets", the films were manufactured having a thickness of 100 μm. The films were made of a stack $(X)_p$ having p recurring units of X with:

- p equal to: 2, 32, 64, 128, 256 and 2048 (or 2^n units of X with n equal to 1, 5, 6, 7, 8 and 11).
- X equal to:
  a) b = PA6;
  b) b = EVOH; and
  c) a/b/a = PA6/EVOH/PA6 (microlayers of PA6 and EVOH with the thicknesses relatively equal to 90/10, 70/30, 50/50, 30/70, and 10/90).

II) Tests made and the results obtained:

A) Mechanical characteristics

The tested samples were prepared according to the standard US ASTM D1708. The samples had been placed in a dessicator and conditioned with an atmosphere at 54% relative humidity before passage on the traction machine (Instron model 1123), at a displacement speed of the cross-head at 10 mm-min^{-1}.

The resulting curves for the stress in megapascals ("MPa") versus strain (%) are shown in Figures 1-3. Figure 1 corresponds to a film $(PA6)_p$, Figure 2 to a film $(EVOH)_p$ and Figure 3 to a film (PA6/EVOH/PA6) having a 50/50 PA6/EVOH volumetric composition. The different values of n are also shown in the Figures 1-3.

B) Resistance to puncture:

The resistance to puncture was measured on a traction machine (Instron model 4204) on samples conditioned in an atmosphere at 50% relative humidity. The sample film was fixed on a circular support of 2.54 mm in diameter. The girder consisted of a

hemispherical head having a diameter of 0.65 mm and displaced at a speed of 2.54 mm-min^{-1}. Figure 6 shows the resistance to puncture (in MPa) of the films as a function of the number of microlayers. The films tested were of the type $(EVOH)_p$, $(PA6)_p$, $(PA6/EVOH/PA6)_p$ having a volumetric composition of 50-50 and 90-10.

C) Resistance to flex cracking:

The resistance to flex cracking test is useful for comparing the resistance of the film to usual manipulation and transport and was implemented according to the ASTM E-392 standard. The test is conducted as follows. Using a film sample, a cylinder is formed that is 20.32 cm long and 8.9 cm in diameter and is subjected to a torsion of 360° and a compression up to a length of 3.84 cm. This torsion and compression is done 250 times in 5 minutes to cause flex lines in the material. The film is then examined using coloring agents that reveal holes and cracks which are then counted. Figure 4 shows the number of holes as a function of the number of microlayers, for four films: film I of the type $(EVOH)_p$, film II of the type $(PA6)_p$ and two films III and IV of the type $(PA6/EVOH/PA6)_p$ having volumetric compositions of 50-50 and 90-10, respectively.

D) Measure of the permeability to oxygen:

A measurement of the oxygen permeability of the films was made on an OxTran 1000 gas permeability device according to the ASTM D-3985 standard. The tests were done with gas (nitrogen and oxygen) at roughly no relative humidity.

Figure 5 shows the permeability of oxygen (cm^3-cm/m^2-day-atm) as a function of the number of microlayers for the same four films as shown in Figure 4 as I-IV.

E) Measure of the crystallinity of the materials in the films:

The enthalpies of fusion (in J/g) for each of the films were obtained. From the enthalpies of fusion in J/g obtained from the diagrams of differential enthalpy (differential scanning calorimetry or DSC), the values were measured relative to two different materials that are generally distinct on a same diagram, as shown in Figures 11 and 12. The crystallinity (in %) is generally given by the relationship: (enthalpy of fusion measured) / (enthalpy of fusion of the same 100% crystalline material) x 100. The enthalpies of fusion are given by the literature as 117 J/g for EVOH and 191 J/g for PA6.

EXAMPLE SET 2

The following films were manufactured having a thickness of 300 μm:

a) a film having 5 layers PE/Adh/EVOH/Adh/PE with the relative thicknesses of PE, adhesive (Adh) and EVOH corresponding respectively to 77%, 15%, and 8% of the total thickness;

b) a material $(a/b/a)_p$ according to the invention where a/b/a is equal to PE/EVOH/PE and p equals 256.

Film b exhibits mechanical characteristics that are noticeably superior as compared to Film a. For example, the resistance to fracture was measured as 17 MPa for Film b versus 15 MPa for Film a. Further, Film b had an elongation of 300% versus 270% for Film a. Other properties are roughly similar. However, it was observed that even without the adhesive in Film b, there was no tendency to delaminate.

EXAMPLE SET 3

Films having a thickness of 30 μm were made from a stack $(X)_p$ of microlayers using EVOH with the goal of making films corresponding to the type "A/D/$(X)_p$/E/C". These films had a thickness of 60 μm with the layers A and B being layers of PE having thicknesses of 12.5 μm and the layers D and E being layers of adhesive deposited by coating having thicknesses of 2.5 μm.

It was observed that the films, according to the present invention, had properties roughly similar to those of the standard films. The standard films consist of, at the location of the stack $(X)_p$, three layers of PA6/EVOH/PA6. The thickness of the layer of EVOH is 30 μm and the thickness of each layer of PA6 is 12 μm.

CONCLUSIONS

Films having microlayers have a number of advantageous properties as compared to standard materials. First, the stress-strain curves show a significant improvement of the mechanical characteristics of the films with an increasing number of identical microlayers when the microlayers are made of EVOH, PA6 or some mixture of the two. Further, the results indicate that there is a positive synergistic effect between PA6 and

EVOH when microlayers are made using those two materials. In addition, there are increases in the resistances to puncture and flex cracking for the mixed EVOH/PA6 materials, which may also be caused by positive synergistic effects between the two materials.

The permeability of the materials, however, varies only slightly for PA6 and actually increases slightly for EVOH. Further, as the number of microlayers increases, the permeability tends to increase as well. It has been found that the crystallinity of the EVOH tends to decrease with increasing numbers of microlayers, thereby causing an increase in the permeability of the material to oxygen.

In general, the invention makes it possible to obtain more economical films or materials because of the removal of certain layers (for example, by replacing PA6/EVOH/PA6 by a stack $(X)_p$ of microlayers of EVOH), or the layers' replacement by a layer of an already used and less costly material such as, for example, removing the adhesive layers of PE/Adh/EVOH/Adh/PE and replacing them by the material $(a/b/a)_p$.

It should be understood that various changes and modifications to the presently preferered embodiments described herein will be apparent to those skilled in the art. Such changes and modifications may be made without departing from the spirit and scope of the present invention and without diminishing its attendant advantages. It is, therefore, intended that such changes and modifications be covered by the appended claims.

CLAIMS

1. A multilayer film comprising a stack of recurring units wherein each recurring unit has at least one extruded microlayer of a first thermoplastic material, characterized in that the first thermoplastic material forms a barrier against oxygen, said first thermoplastic material being selected from the group consisting of EVOH, polyketones, polyamides, PVDC, PLC, polyvinylalcohol, said film having a total thickness of between 10 and 2 500 μm.

2. The film of Claim 1 wherein the first thermoplastic material forms a barrier against water vapor.

3. The film of Claim 1 wherein the plurality of recurring units includes a second thermoplastic material.

4. The film of Claim 3 wherein the first thermoplastic material forms a first microlayer and the second thermoplastic material forms a second microlayer wherein the first and second microlayers are coextruded and form the recurring units within the stack.

5. The film of Claim 3 wherein the plurality of recurring units includes a third material wherein the first thermoplastic material forms a first microlayer, the second thermoplastic material forms a second microlayer and the third thermoplastic material forms a third microlayer wherein each unit consists of each of the first, second and third microlayers.

6. The film of Claims 4 or 5 wherein at least one of the thermoplastic materials is selected from the group consisting of polyamide, polyethylene and polypropylene.

7. The film of Claims 4 or 5 further comprising:

at least one adhesive microlayer between the first and second microlayers in each recurring unit wherein the adhesive microlayer bonds the first microlayer to the second microlayer.

8. The film of Claim 5 further comprising:

a first adhesive microlayer between the first and second microlayers in each recurring unit wherein the adhesive microlayer bonds the first microlayer to the second microlayer; and

a second adhesive microlayer between the second and third microlayers in each reucrring unit wherein the second adhesive microlayer bonds the second microlayer to the third microlayer.

9. The film of Claim 3 wherein each recurring unit includes at least one microlayer formed from a mixture of the first and second thermoplastic materials.

10. The film of any of Claims 1-9 further comprising:

an external layer disposed on a surface of the stack of microlayers.

11. The film of Claim 10 wherein the external layer is selected from the group consisting of polyamide, polyethylene and polypropylene.

12. The film of Claim 10 further comprising:

an external adhesive layer disposed between the external layer and the stack of microlayers wherein the external adhesive layer bonds the external layer to the stack of microlayers.

13. The film of Claim 1 wherein the polyamide barrier against oxygen is selected from the group consisting of PA6 and MXD6.

14. The material of Claim 2 wherein the barrier against water vapor is selected from the group consisting of polyethylene, polypropylene, thermoplastic polyester, polyvinyl chloride, polyvinylidene chloride and polyethylene terephthalate.

15. The film of Claims 7 or 8 wherein the adhesive microlayers are partially soluble at the same time to the microlayers surrounding the adhesive microlayers.

16. The film of Claims 3 or 9 wherein the first and second thermoplastic materials are selected from the group consisting of polyamide and ethylene-vinyl alcohol copolymer.

17. The film of claims 1 to 16 wherein said first thermoplastic material has a crystallinity of at least 50%.

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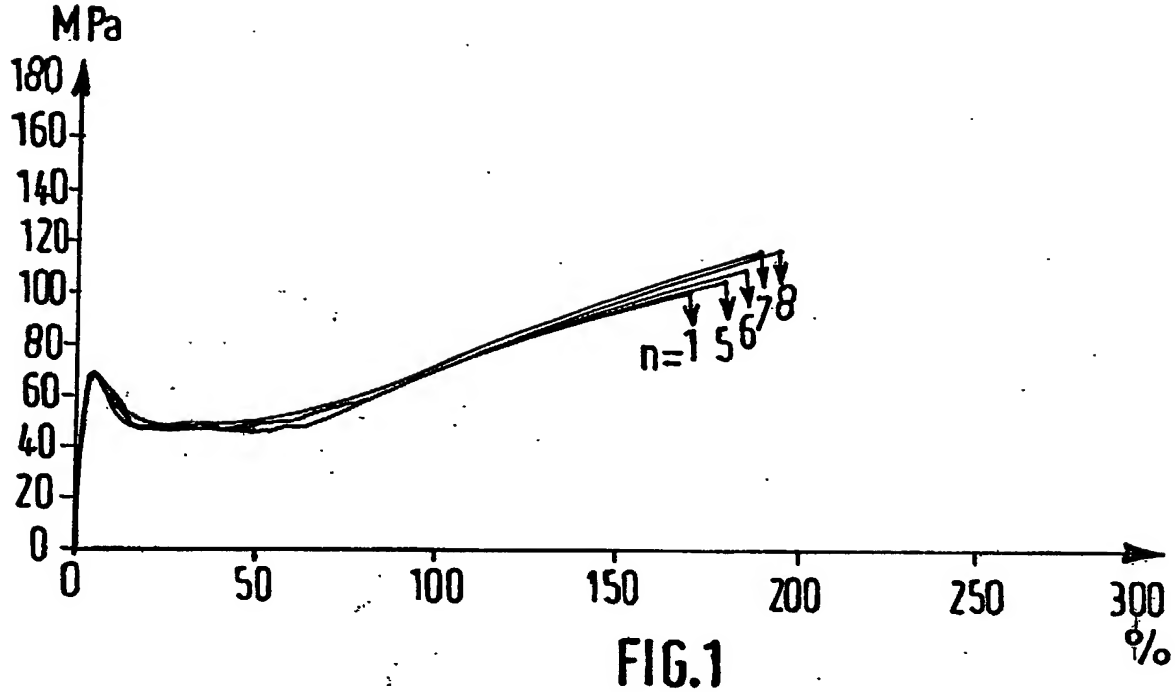
(54) Title: BARRIER MATERIAL MADE OF EXTRUDED MICROLAYERS

(57) Abstract: A multilayer film comprising: a stack of recurring units wherein each recuring unit has at least one extruded microlayer of a first thermoplastic material and further wherein the first thermoplastic material forms a barrier against oxygen wherein the film has a total thickness of between 10 and 2500 μm. If more than one microlayer is contained within each unit, then the microlayers may be coextruded together. Specifically, the barrier microlayer may be selected from among EVOH, polyketones, PA6, MXD6, PVDC, LCP, polyvinyl alcohol ("PVOH") or any other like barrier material against oxygen.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100
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300
%
n=1 5 6 7 8

FIG.1

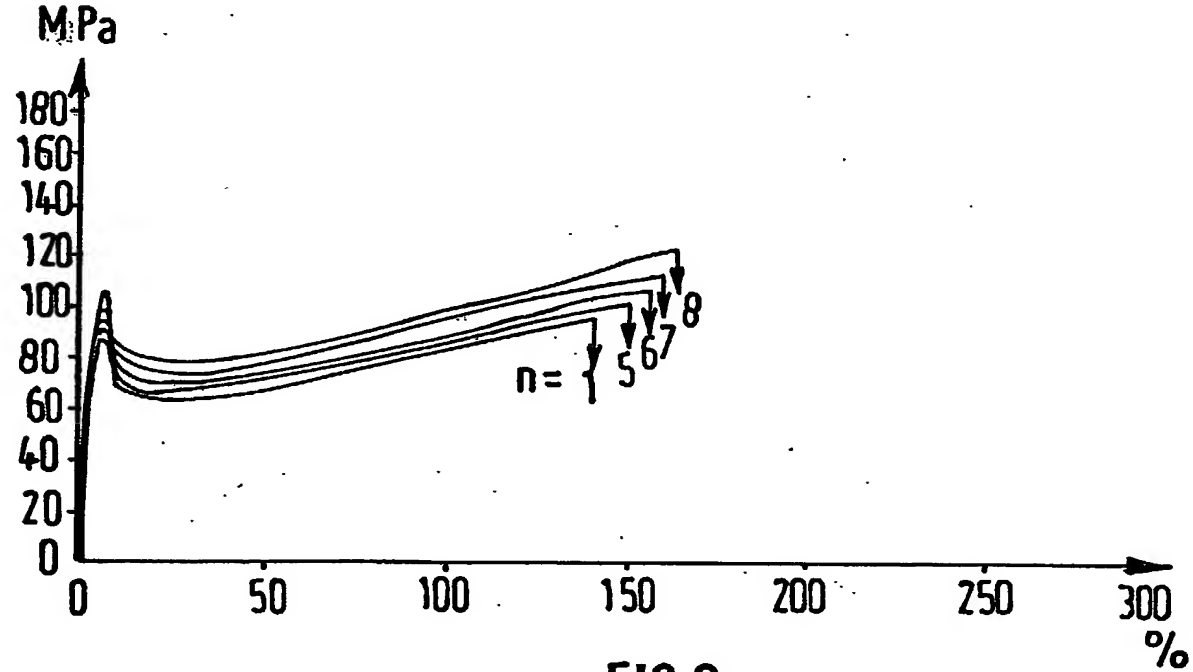
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FIG.2

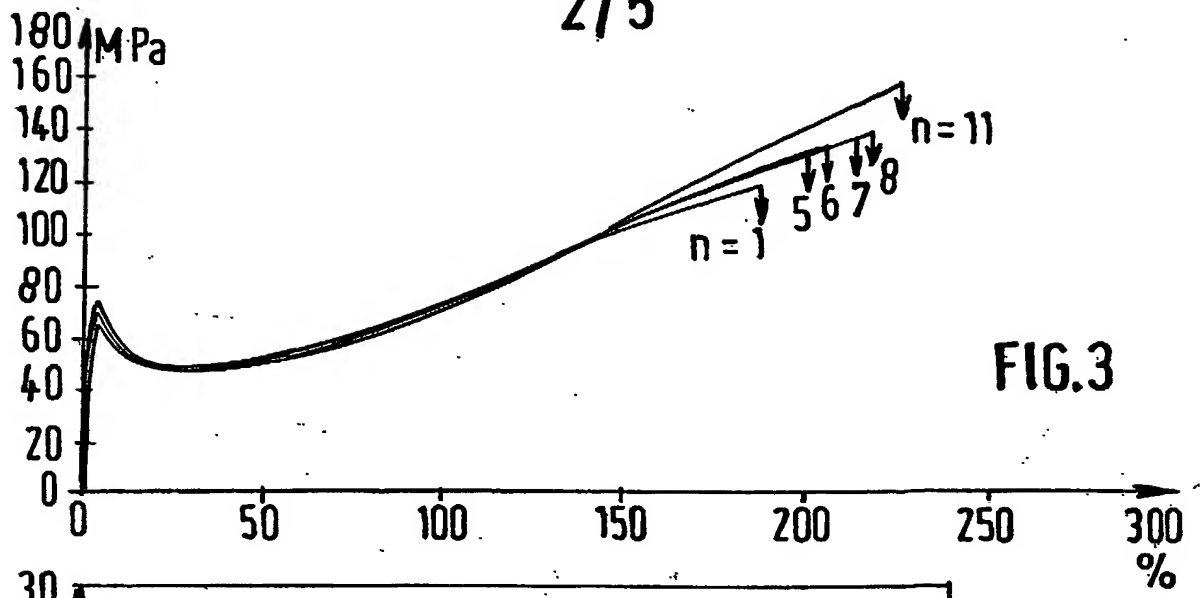


FIG.3

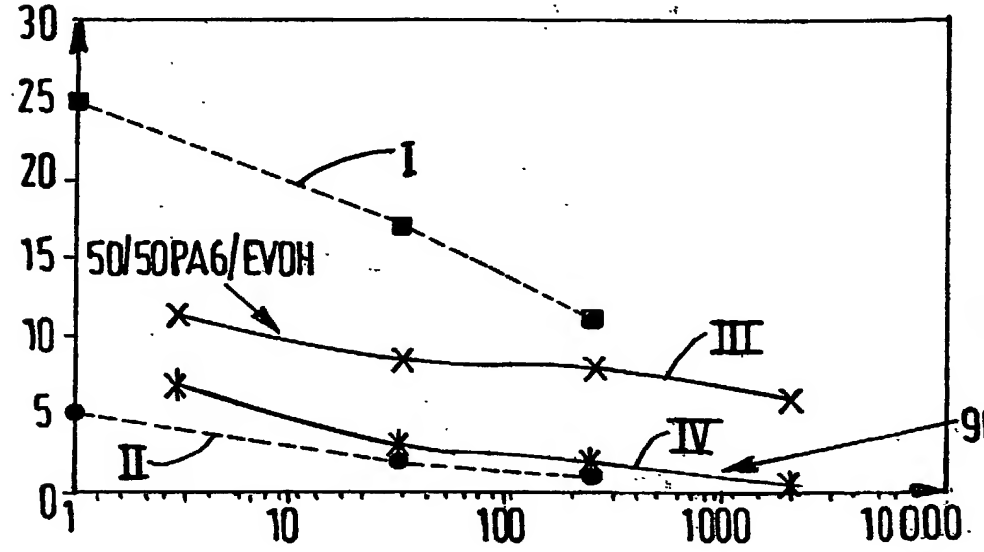


FIG.4

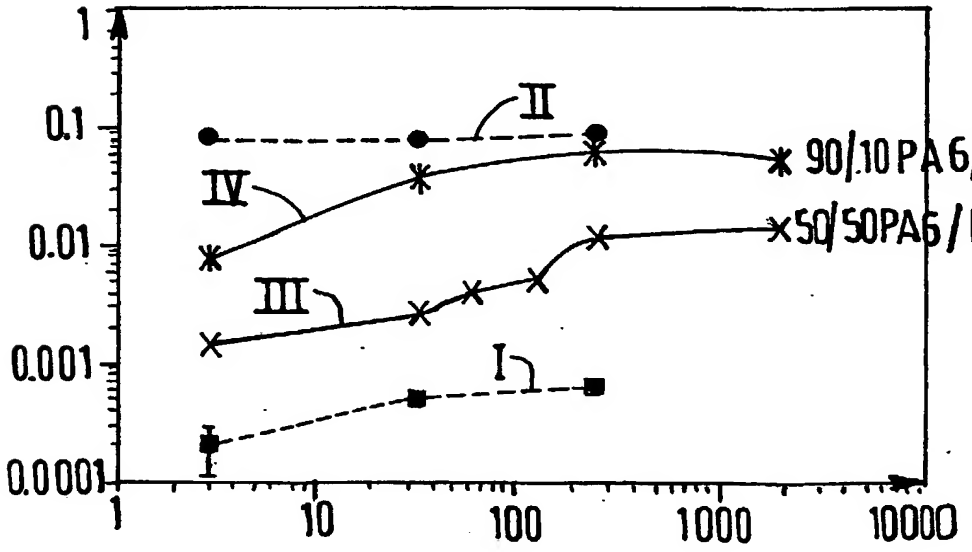
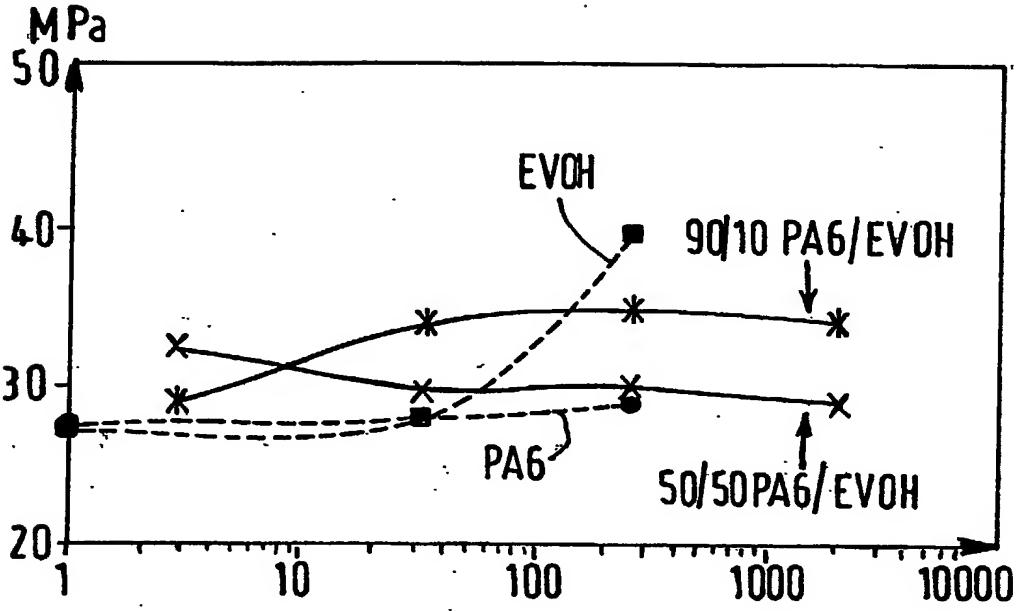


FIG.5


MPa
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20
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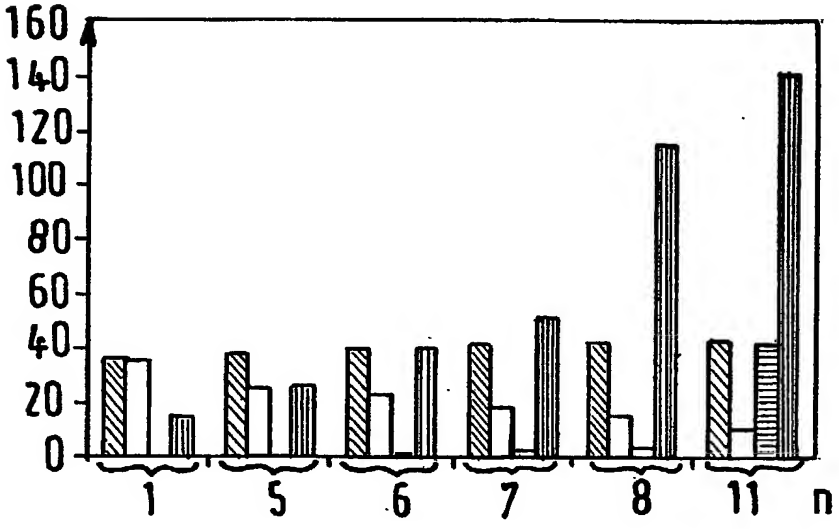
10
100
1000
10000
EVOH
90/10 PA6/EVOH
PA6
50/50PA6/EVOH

FIG.6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n

FIG.7

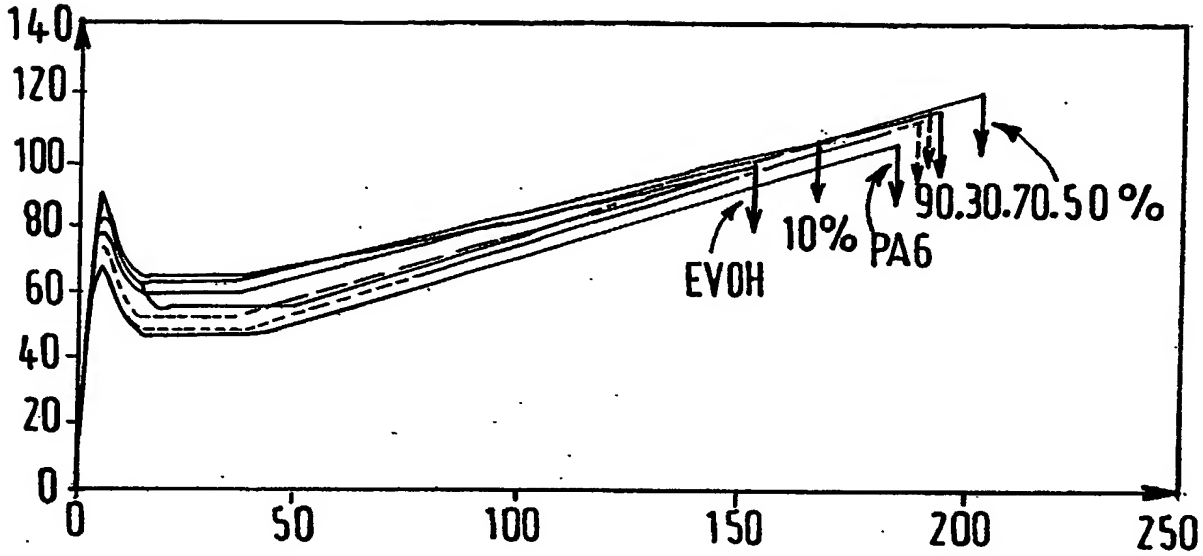

FIG.8

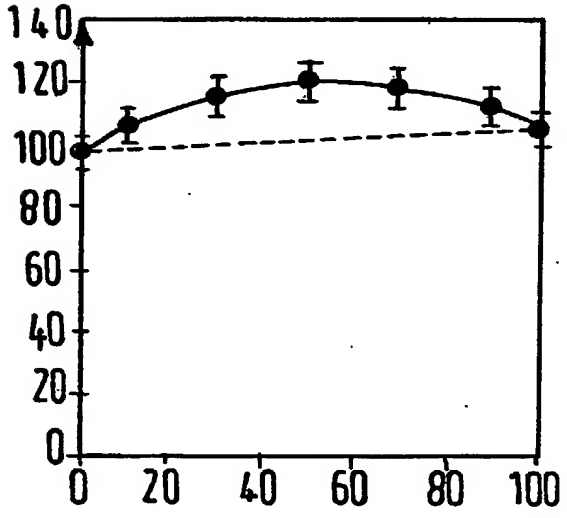

FIG.9

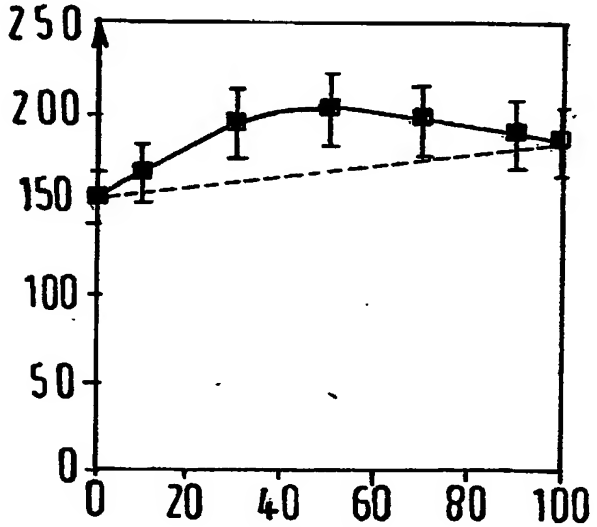

FIG.10

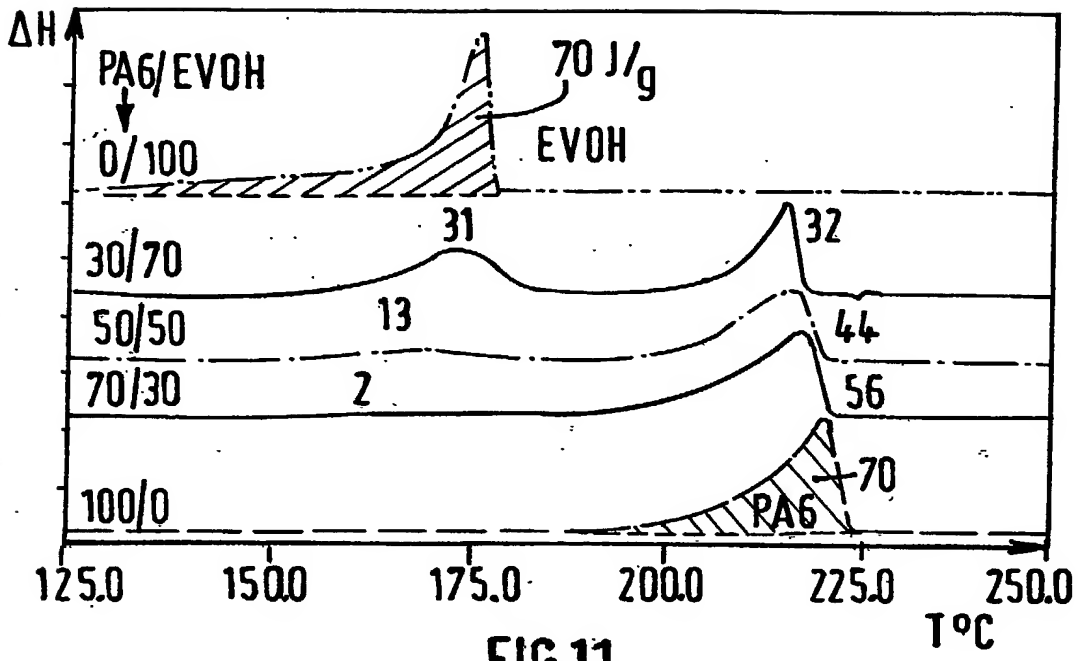
ΔH
PA6/EVOH
0/100
70 J/g
EVOH
30/70
31
32
50/50
13
44
70/30
2
56
100/0
70
PA6
125.0
150.0
175.0
200.0
225.0
250.0
T°C

FIG.11

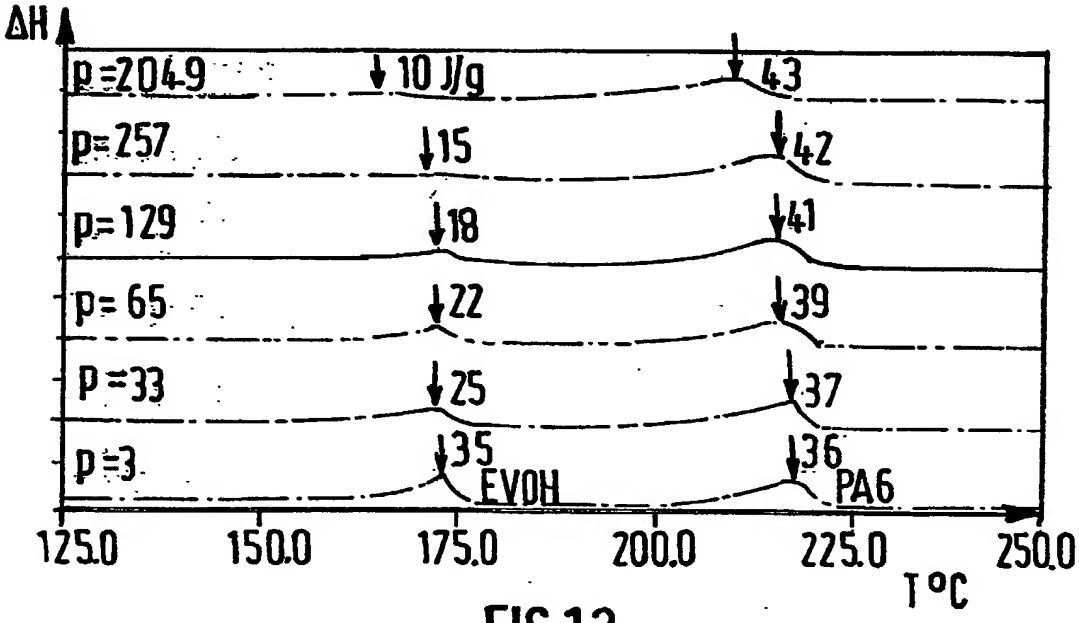
ΔH
p=204.9
10 J/g
43
p=257
15
42
p=129
18
41
p=65
22
39
p=33
25
37
p=3
35
EVOH
36
PA6
125.0
150.0
175.0
200.0
225.0
250.0
T°C

FIG.12

PATENT Docket No. 24180-653001

COMBINED DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I/We hereby declare that

This declaration is of the following type:

☐ original ☐ design ☐ supplemental
☒ national stage of PCT
☐ divisional ☐ continuation ☐ continuation-in-part

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

BARRIER MATERIAL MADE OF EXTRUDED MICROLAYERS

the specification of which:

☐ is attached hereto.
☒ was filed on December 11, 2001 as Application No. _____ and was amended on _____ *(if applicable)*.
☐ was described and claimed in PCT International Application No. _____ filed on _____ and was amended under PCT Article 19 on _____ *(if any)*.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate or under 365(a) of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT International application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

COUNTRY	APPLICATION	DATE OF FILING *(day,month,year)*	PRIORITY CLAIMED			
				YES		NO
				YES		NO

I hereby claim the benefit pursuant to Title 35, United States Code, § 119(e) of the following United States provisional application(s):

PRIOR U.S. PROVISIONAL APPLICATIONS CLAIMING THE BENEFIT UNDER 35 USC 119(e)	
APPLICATION NO.	DATE OF FILING *(day,month,year)*

☐ Additional provisional application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto.

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or 365(c) of any PCT international application(s) designating the United States of America listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 USC 120					
U.S. APPLICATIONS			Status *(check one)*		
U.S. APPLICATIONS	U.S. FILING DATE		PATENTED	PENDING	ABANDONED
1.					
2.					
3.					
PCT APPLICATIONS DESIGNATING THE U.S.			Status *(check one)*		
PCT APPLICATION NO.	PCT FILING DATE	U.S. SERIAL NOS. ASSIGNED *(if any)*	PATENTED	PENDING	ABANDONED
4. PCT/IB00/00934	6 JUNE 2000			X	
5.					
6.					

DETAILS OF FOREIGN APPLICATIONS FROM WHICH PRIORITY CLAIMED UNDER 35 USC 119 FOR ABOVE LISTED U.S./PCT APPLICATIONS				
ABOVE APPLN. NO.	COUNTRY	APPLICATION NO.	DATE OF FILING *(day,month,yr)*	DATE OF ISSUE *(day,month,yr)*
1.				
2.				
3.				
4. PCT/IB00/00934	France	99/07641	June 11, 1999	
5.				
6.				

I hereby appoint Joseph H. Paquin, Jr. (Reg. No. 31,647), Margaret M. Duncan (Reg. No. 30,879), John G. Bisbikis (Reg. No. 37,095), Matthew E. Leno (Reg. No. 41,149), Stephen T. Scherrer (Reg. No. 45,080) and Patrick D. Richards (Reg. No. 48,905) members of the bar of the State of Illinois, and Joy Ann G. Serauskas (Reg. No. 27,952) of the firm McDermott, Will & Emery using the address 227 West Monroe Street, Chicago, Illinois 60606-5096 (Telephone 312/372-2000), my attorneys and/or agent, with full power of substitution and revocation, to prosecute this application, and to transact all business in the Patent and Trademark Office connected therewith. It is requested that all correspondence be directed to:

Stephen T. Scherrer
McDERMOTT, WILL & EMERY
227 West Monroe Street
Chicago, Illinois 60606-5096

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full name of **sole or first inventor**: Sandrine Tournier 1-00

Inventor's Signature: 

Date: January 28, 2002

Residence: 50 rue Jean Pain
38600 Fontaine FRY
FR

Post Office Address: Same as above

Citizenship: French

Full name of **second joint inventor**, if any: Chad David Mueller 2-00

Inventor's Signature: *Executed Separately*

Date:

Residence: 405 South Olde Onedia Street WI
Apartment 413
Appleton, Wisconsin 54911
US

Post Office Address: Same as above

Citizenship: US

Full name of **third joint inventor**, if any: Roger L. Kaas 3-00

Inventor's Signature: *Executed Separately*

Date:

Residence: 1830 Eagle Drive WI
Neenah, Wisconsin 54956
US

Post Office Address: Same as above

Citizenship: US

Full name of **fourth joint inventor**, if any: Alain Jupin 4th

Inventor's Signature: X

Date: X February 4 2002

Residence: 19. rue des Rondes
51800 Sainte Menehould
FR

Post Office Address: Same as above

Citizenship: French

Full name of **fifth joint inventor**, if any: Bertrand Fillon 5th

Inventor's Signature: X

Date: X January 28 2002

Residence: 42, Allée des Noisettes
38340 Voreppe
FR

Post Office Address: Same as above

Citizenship: French

PATENT Docket No. 24180-653001

COMBINED DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I/We hereby declare that

This declaration is of the following type:

☐ original ☐ design ☐ supplemental
☒ national stage of PCT
☐ divisional ☐ continuation ☐ continuation-in-part

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

BARRIER MATERIAL MADE OF EXTRUDED MICROLAYERS

the specification of which:

☐ is attached hereto.
☒ was filed on December 11, 2001 as Application No. _____ and was amended on _____ *(if applicable)*.
☐ was described and claimed in PCT International Application No. _____ filed on _____ and was amended under PCT Article 19 on _____ *(if any)*.

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COUNTRY	APPLICATION	DATE OF FILING *(day,month,year)*	PRIORITY CLAIMED			
				YES		NO
				YES		NO

I hereby claim the benefit pursuant to Title 35, United States Code, § 119(e) of the following United States provisional application(s):

PRIOR U.S. PROVISIONAL APPLICATIONS CLAIMING THE BENEFIT UNDER 35 USC 119(e)	
APPLICATION NO.	DATE OF FILING *(day,month,year)*

☐ Additional provisional application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto.

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PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 USC 120					
U.S. APPLICATIONS		Status *(check one)*			
U.S. APPLICATIONS	U.S. FILING DATE	PATENTED	PENDING	ABANDONED	
1.					
2.					
3.					
PCT APPLICATIONS DESIGNATING THE U.S.			Status *(check one)*		
PCT APPLICATION NO.	PCT FILING DATE	U.S. SERIAL NOS. ASSIGNED *(if any)*	PATENTED	PENDING	ABANDONED
4. PCT/IB00/00934	6 JUNE 2000			X	
5.					
6.					

DETAILS OF FOREIGN APPLICATIONS FROM WHICH PRIORITY CLAIMED UNDER 35 USC 119 FOR ABOVE LISTED U.S./PCT APPLICATIONS				
ABOVE APPLN. NO.	COUNTRY	APPLICATION NO.	DATE OF FILING *(day,month,yr)*	DATE OF ISSUE *(day,month,yr)*
1.				
2.				
3.				
4. PCT/IB00/00934	France	99/07641	June 11, 1999	
5.				
6.				

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Stephen T. Scherrer
McDERMOTT, WILL & EMERY
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Chicago, Illinois 60606-5096

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Full name of **sole or first inventor**: Sandrine Tournier

Inventor's Signature: *Executed Separately*

Date:

Residence: 5, rue Jean Pain
38600 Fontaine
FR

Post Office Address: Same as above

Citizenship: French

Full name of **second joint inventor**, if any: Chad David Mueller

Inventor's Signature: Chad David Mueller

Date: 12/18/01

Residence: 405 South Olde Onedia Street
Apartment 413
Appleton, Wisconsin 54911
US

Post Office Address: Same as above

Citizenship: US

Full name of **third joint inventor**, if any: Roger L. Kaas

Inventor's Signature: *Executed Separately*

Date:

Residence: 1830 Eagle Drive
Neenah, Wisconsin 54956
US

Post Office Address: Same as above

Citizenship: US

Full name of **fourth joint inventor**, if any: Alain Jupin

Inventor's Signature: *Executed Separately*

Date:

Residence: 19, rue des Rondes
51800 Sainte Menehould
FR

Post Office Address: Same as above

Citizenship: French

Full name of **fifth joint inventor**, if any: Bertrand Fillon

Inventor's Signature: *Executed Separately*

Date:

Residence: 42, Allée des Noisettes
38340 Voreppe
FR

Post Office Address: Same as above

Citizenship: French

PATENT
24180-653001

Docket No.

COMBINED DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I/We hereby declare that

This declaration is of the following type:
☐ original ☐ design ☐ supplemental
☒ national stage of PCT
☐ divisional ☐ continuation ☐ continuation-in-part

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BARRIER MATERIAL MADE OF EXTRUDED MICROLAYERS

the specification of which:
☐ is attached hereto.
☒ was filed on December 11, 2001 as Application No. _____ and was amended on _____ *(if applicable)*.
☐ was described and claimed in PCT International Application No. _____ filed on _____ and was amended under PCT Article 19 on _____ *(if any)*.

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COUNTRY	APPLICATION	DATE OF FILING *(day,month,year)*	PRIORITY CLAIMED			
				YES		NO
				YES		NO

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PRIOR U.S. PROVISIONAL APPLICATIONS CLAIMING THE BENEFIT UNDER 35 USC 119(e)	
APPLICATION NO.	DATE OF FILING *(day,month,year)*

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PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 USC 120					
U.S. APPLICATIONS			**Status** *(check one)*		
U.S. APPLICATIONS	**U.S. FILING DATE**		**PATENTED**	**PENDING**	**ABANDONED**
1.					
2.					
3.					
PCT APPLICATIONS DESIGNATING THE U.S.			**Status** *(check one)*		
PCT APPLICATION NO.	**PCT FILING DATE**	**U.S. SERIAL NOS. ASSIGNED** *(if any)*	**PATENTED**	**PENDING**	**ABANDONED**
4. PCT/IB00/00934	6 JUNE 2000			X	
5.					
6.					

DETAILS OF FOREIGN APPLICATIONS FROM WHICH PRIORITY CLAIMED UNDER 35 USC 119 FOR ABOVE LISTED U.S./PCT APPLICATIONS				
ABOVE APPLN. NO.	**COUNTRY**	**APPLICATION NO.**	**DATE OF FILING** *(day,month,yr)*	**DATE OF ISSUE** *(day,month,yr)*
1.				
2.				
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4. PCT/IB00/00934	France	99/07641	June 11, 1999	
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Stephen T. Scherrer
McDERMOTT, WILL & EMERY
227 West Monroe Street
Chicago, Illinois 60606-5096

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full name of **sole or first inventor**: Sandrine Tournier

Inventor's Signature: *Executed Separately*

Date: _____

Residence: 5, rue Jean Pain
38600 Fontaine
FR

Post Office Address: Same as above

Citizenship: French

Full name of **second joint inventor**, if any: Chad David Mueller

Inventor's Signature: *Executed Separately*

Date: _____

Residence: 405 South Olde Onedia Street
Apartment 413
Appleton, Wisconsin 54911
US

Post Office Address: Same as above

Citizenship: US

Full name of **third joint inventor**, if any: Roger L. Kaas

Inventor's Signature: Roger L Kaas

Date: Dec. 12, 2001

Residence: W4840 Escarpment Terrace
Sherwood, WI 54169
US

Post Office Address: Same as above

Citizenship: US

Full name of **fourth joint inventor**, if any: Alain Jupin

Inventor's Signature: *Executed Separately*

Date: _____

Residence: 19, rue des Rondes
51800 Sainte Menehould
FR

Post Office Address: Same as above

Citizenship: French

Full name of **fifth joint inventor**, if any: Bertrand Fillon

Inventor's Signature: *Executed Separately*

Date: _____

Residence: 42, Allée des Noisettes
38340 Voreppe
FR

Post Office Address: Same as above

Citizenship: French